Study of Liquid smoke Formation in Waste of patchouly oil (*Pogostemon Cablin* Benth) Pyrolysis Kinetics

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ABSTRACT

Liquid smoke is a substance produced from smoke passed through a tube from a combustion chamber filled with select wood chips to a condenser. In the condenser, the smoke cools and forms a liquid, aided by the addition of water. Pyrolysis is an attractive thermal conversion technology used to produce bio-oil, char and gas. Pogostemon Cablin Benth *pyrolysis in general involves a complex set of chemical reactions. Overall, this research work represents a comprehensive and thorough thermo kinetic study of Pogostemon Cablin* Benth *pyrolysis that approaches the thermal behavior by recognizing the connections between different chemical phenomena making up the pyrolytic process. In this study, we investigated the pyrolysis of Pogostemon Cablin* Benth *under* N_2 *atmosphere at various temperatures between 250 to 500°C in a fixed bed reactor completed with heater, balance, cyclone and condenser. Fluid bed pyrolysers give good and consistent performance with high liquid yields of typically 23%wt. from Pogostemon Cablin* Benth *on a dry feed basis. On the other hand, this research was intended to produce correlations for residence time (t) with devolatilization degree or values of volatile matter conversion* (x_s)*. The results of volatile matter conversion have also shown a good agreement between the values prediction by the model and those obtained experimentally. The highest volatile matter conversion in this research was 82%, and this was obtained at process conditions of temperature of 450°C, Pogostemon Cablin* Benth *particles 10 mesh.*

Key Words: pyrolysis, liquid smoke, kinetic, *Pogostemon Cablin* Benth

Acknowledgements
Authors are grateful for financial support from DP2M DIKTI (Hiber scheme)

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Introduction

Indonesia has many kind of patchouly which were the largest in the world, more than 90% of its kind could be found in Indonesia. Processing of liquid smoke by means of pyrolysis produces solid residue (charcoal), tar and gasses. The boundaries for developing Patchouly Waste decomposition by pyrolysis were limited kinetic data and decision for thorough reaction rate equation. It was mainly caused by complex interconnection bwtween parameters affecting the reaction. Nevertheless, the assumptions used to formulate model were high in variation (Trianna dan Rochimullah, 2003). The different approach used resulted in different decompotition reaction rate model formulated by individual research (Trianna dan Mulyadi, 2006). Up to date, kinetic model and empirical equation formulated by previous research mostly used model mechanism of progressive-conversion model. Therefore, formulation of reaction rate equation could be approached by pseudo homogenous reaction model.

THEORY

1. Kinetic Formulation of Decomposition Rate

By assuming that the diffusion to release vapor resulted from pyrolysis reaction happened spontaneously and mass transfer barrier could be ignored, then the overall reaction rate equation was limited by chemical reaction. Therefore decomposition was happened by *progressive-conversion model.* Reaction rate stated in mass fraction per time could be written as:

$$dC/dt = - k_h (C - C_\infty)^n$$

with τ = time needed for solid, tar and gas residuea become constant (i.e. at $m = m_\infty$),

n = reaction order,

k_h = constant for pseudo homogenous rate reaction, $minutes^{-1}$

Application of equation, which was generally done by first order approach, defines that infinite time (τ) was needed to make solid, tar and gas residues become constant. The value of τ calculated starting when isothermal process began and the value

of m_∞ was not affected by heating rate but by isothermal temperature. Based on theory by Arrhenius, could be written as:

$$dC/dt = -k_o\, e^{-E/RT}\, (C - C_\infty)^n \quad ,$$

The equation follows first order reaction equation, therefore:

$$dC/dt = -k_o\, e^{-E/RT}\, (C - C_\infty)$$

In isothermal process, integration of that equation with boundary condition between t = 0 to t = t, obtained:

$$\ln (1 - C_\infty) - \ln(C - C_\infty) = k_o\, e^{-E/RT}\, (t)$$

or; $\ln (m_t - m_\infty) = \ln(m_{to} - m_\infty) - k\, t$

2. Empirical formulation of decomposition rate

This formulation was generally done by exponential or polynomial model approach. Empirical formulation of decomposition rate was initially done by Badzioch and Hawksley by simulation using Gauss distributioin model and defined that:

C = matter volatile mass normalization, which $C = m_t/m_{to}$,
C_∞ = matter normalisation at $t = \tau$, which $C_\infty = m_\infty/m_{to}$
m_{to}= waste mass at initial isothermal temperature, gram,
m_t = residue mass at time = t, gram,
m_∞ = residue mass at $t = \tau$ at isothermal temperature, gram,

then:

$$-[dC/dt] = k_1\, C + k_2\, C^3$$

Next step was developed by mulyadi (2010), by formulating:

$m_t = m_{to}\, e^{(-k't)}$, then decomposition rate can be written:

$$-[dm_t/dt] = k'\, m_{to}\, e^{(-k' t)}$$

At t=t, *volatile matter* fraction that decomposed reached (x_s),

$$x_s = [m_{to} - m_t]/ [m_{to} - m_\infty]$$

Trianna and Rochimullah (2002) done *unreacted core* model research (heterogen reaction) but was limited at first order reaction rate equation. The mathematic formulation model of decomposition reaction developed by Trianna and Mulyadi (2006) resulted in functional relation between convertion and reaction time stated by:

$$x_s = -0{,}0152 + 0{,}1179\, t^{0{,}5}.$$

By substituting that equation then obtained:

$$-\ln [(1- x_s)] = k\,t$$

If the reaction has been control, and reaction mechanism follow the constant size particles, and taking place in unreacted-core model, then

$$-(1/a)[(dC)/dt] \quad = k\,C_\infty = -[1/(a.m_{to})][dm_t/dt] \qquad (1).$$

By assuming solid particle was a sphere with equal size equation (1) become;

$$-dr/dt = k(m_{to}/\rho)\,C_\infty,$$

$$t = [(r_o\,\rho)/(m_\infty\,k)](1 - r/r_o) \qquad (2)$$

or $$r/r_o \quad = (1-x_s)^{1/3} \qquad (3).$$

By substituting (2) to (3):

$$[1-(1-x_s)^{1/3}] = [(m_\infty\,k)/(r_o\,\rho)]\,t = [1/\tau]\,t \qquad (4)$$

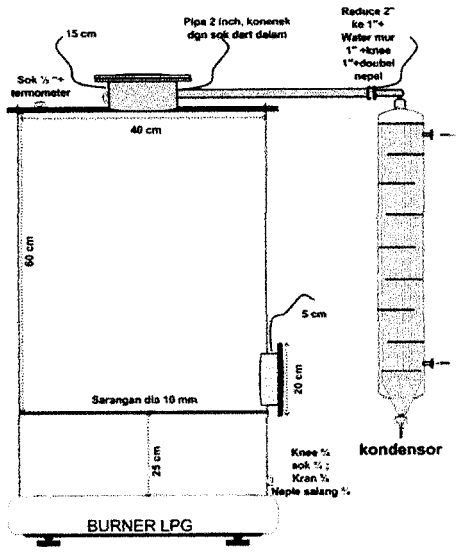
Material and Method

Patchouly Waste as raw material used was obtained from belik–trawas-mojokerto. After being sun dried and separated it was then sieved according to diameter used in experiments. Patchouly Waste was dried under the sun until water content reached 15%. The Patchouly Waste oil was analyzed for water content, ash content, volatile matter, and fixed carbon, consecutively using method of ASTM D 3302-97 a, ASTM D 3174-97, and ASTM D3175-89a. Other method used to determine water content was by heating the Patchouly Waste inside oven at 110°C. It was then cooled down in exicator and weighed until reached constant weight. The Changes in weight is the water content inside patchouly waste. Analysis result shows that water content was 11 %, Size of patchouly waste beads was determined by standard sieving *teyler*. patchouly waste was crushed and sieved. The smallest sieving size was 10 mm, while the largest was 40 mm. Variations of bead size studied were 1, 4, 10, 20, and 40 mm.

Unit for pyrolisis was showed in figure 1. The reactor where pyrolisis took place was made from rust resistance steel. Tar cooler made from stainless steel and gas vessel was made from polyethylene/glass.

Research procedure, patchouly waste of certain size and weight was put into reactor. Heater then turned on. Time (t) was counted after the desired temperature reached and reading of weighing/balance was done to measure solid residue mass (m_{to}).

Measurement of solid mass residue (m_t) was done repeatedly after some period of time. Same treatment also valid for the measurement of tar (bio-oil).



Pirolitor Isian bergerak dengan multitube kondensor

Figure 1. Pyrolisis Unit

Result and Discussion

Preliminary experiment was done to obtain the characteristic of heating and cooling of pyrolisis reactor. Heating was done from room temperature up to the highest temperature studied, i.e. 430 °C (figure 2). To reach the mentioned temperature, 50 minutes was needed.

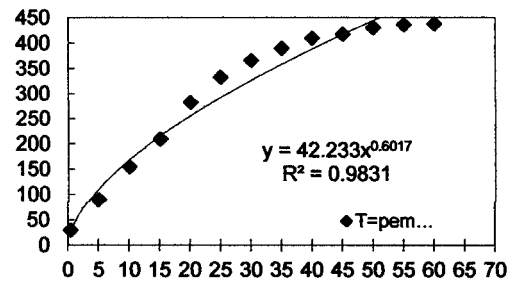


Figure 2. Plot between Heating Temperature and time

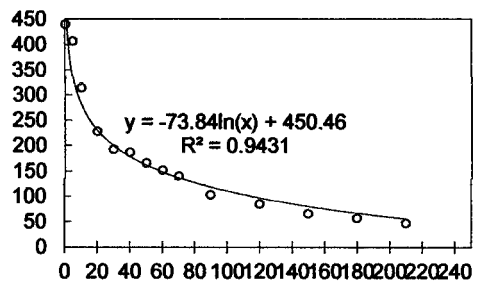


Figure 3. Plot between Cooling Temperature and time

Next, refrigeration of reactor was conducted. Temperature degradation in each moment was shown in figure 3. Hence, collection of result from reactor was done after refrigeration take place for three hours.

patchouly waste used was originated from mbelik-trawas mojokerto. After dried under the sun, it was then separated and sieved according to diameter to be used in research. The raw material was analyzed for water content, ash content, volatile matter, and fixed carbon, consecutively using method of ASTM D 3302-97 a, ASTM D 3174-97, and ASTM D3175-89a. Size of patchouly waste beads was determined by standard sieving *teyler*. Waste patchouly was crushed and sieved.

Relation of Conversion with Time and Temperature, pyrolysis of patchouly waste or conversion of *volatile matter* was calculated by m_{to}, m_t, dan m_∞. To calculate conversion, patchouly waste mass inside reactor (measured as solid residue) was measured at various time and temperature. Conversion of volatile matter or *devolatilization degree* was calculated by $x_s = [m_{to} - m_t]/ [m_{to} - m_\infty]$. The value of $(m_{to} - m_t)$ was the volatilized mass at patchouly waste at every moment and the total mass of patchouly waste that could be volatilized was $(m_{to} - m_\infty)$. Conversion if volatile matter in patchouly waste (x_s) was shown in figure 3. In figure 4, it can be seen that conversion of volatile matter on patchouly waste (x_s) was highly affected by processing time. It was caused by the higher probability of volatile matter to decomposed, therefore x_s increases. However, the rise was no longer seen after 45 minutes of pyrolisis time. Infinite time (τ_{data}) was the time needed to reach constant condition of solid residue, tar and gas. The value of τ_{data} measured after the process reached isothermal to the time at the turf mass inside reactor reahed constant. The value of patchouly waste mass measured as m_∞. Next, the data was used to calculate τ_r using equation:

$$[1-(1-x_s)^{1/3}] = t/\tau_r$$

or $X_1 = t/\tau_r$ with $x_1 = [1-(1-x_s)^{1/3}]$,

According to the effect of t to x_s, the relation between t and x_1 was obtained and shown in figure 5.

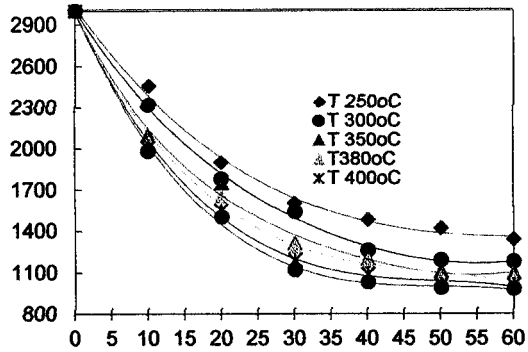


Figure 4. Relaton of x_s and t

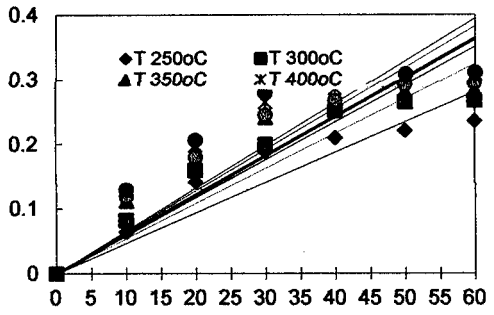


Figure 5. Relation of $[1-(1-x_s)^{1/3}]$ with time

Numurical calculation could be applied to calculate τ_{count}. After τ_{count} determined, the the value of decomposition rate constant (k) could be calculated by equation:

$$\tau_r = [(r_o \rho)/(m_\infty k)] \quad \text{atau} \quad k = [(r_o \rho)/(m_\infty \tau_r)]$$

Result of k value at various temperatures could be correlated well to the unreacted-core model. Doing so, process of Waste patchouly decomposition could be certainly determined that chemical reaction was the control, and following first order reaction. As the effect of time, the rise in pyrolisis temperature caused increase in volatilized matter, thus increase in decomposed fraction (x_s). The rise was caused by increase of volatile matter movement so that collision frequency (k_o) and activation energy (E) rises, therefore decomposition rate constant (k) increase. From the influence of temperature (T) to k, then values of k_o and E could be determined by Arrhenius equation.

Conclusion

1. Rate of reaction controlled by chemical reaction, in the first order, following unreacted-core model
2. Verifying value calculated from correlation of temperature (T) to k, the empiric formulation was: $k = 12(10^{-5})\exp(-5032 / RT)$

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